NOTIZEN

The Bishydridobis(tetrazol-1-yl)borate Anion, $[H_2B(CHN_4)_2]^-$: Synthesis and Structure of the First Tetrazolylborate

Christoph Janiak* and Lothar Esser

Institut für Anorganische und Analytische Chemie, Technische Universität Berlin, Straße des 17. Juni 135, D-10623 Berlin

Z. Naturforsch. **48b**, 394–396 (1993); received September 23, 1992

Bis(tetrazolyl)borate, Azolylborates, Tetrazolylborates, Pyrazolylborates

Potassium bishydridobis(tetrazol-1-yl)borate (**1**) has been synthesized from KBH_4 and tetrazole and characterized spectroscopically. Its crystal structure has been determined. **1** crystallizes in the monoclinic space group $P2_1/n$ with a = 537.8(2), b = 1703.5(9), c = 919.6(3) pm, β = 106.12(3)° and V = 809.4(6)·10^6 pm^3.

Introduction

The poly(pyrazol-1-yl)borate anions $[R_nB(pz)_{4-n}]^-$ (pz = pyrazolyl or C-substituted derivative thereof, n = 0–2, R = non-coordinating substituent) have developed into very popular ligands in coordination chemistry [1] and are widely used as chelating agents in the study of transition-metal [2] or main-group elements [3]. Also, the chelate chemistry of analogous ligands, where pyrazolyl is replaced by 1,2,4-triazolyl [4] or benzotriazolyl [5, 6], is recently receiving increased attention. Surprisingly, however, we are not aware of any reference to an azolylborate based on the tetrazole heterocycle.

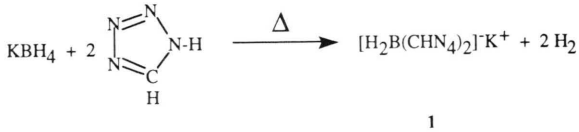
As the chemical properties of complexes containing poly(pyrazolyl)borate ligands may be altered considerably by changes in the substitution pattern of the pyrazolyl ring [1, 2, 6], we attempted the synthesis of the new poly(tetrazolyl)borates with possibly modified electronic properties. In this communication we describe a satisfactory preparation, as well as the structural characterization of potassium bishydridobis(tetrazolyl)borate (**1**), a useful starting material for the preparation of many metal complexes. Furthermore, we note that ligands with a larger number of bonding centers (here three nitrogens in each tetrazolyl ring) are of interest for the development of structure/reactivity models of certain metal-biomolecules and for polyelectronic systems [7].

* Reprint requests to Dr. Christoph Janiak.

Verlag der Zeitschrift für Naturforschung, D-W-7400 Tübingen
0932–0776/93/0300–0394/$ 01.00/0

Results and Discussion

In consonance with earlier reports on the syntheses of poly(azolyl)borates [8], potassium boranate (KBH_4) was found to react with tetrazole (CH_2N_4). When a mixture of KBH_4 and tetrazole is heated to about 100 °C two moles of H_2 are evolved and a white solid is obtained whose elemental analysis is consistent with the potassium bishydridobis(tetrazolyl)borate formula (**1**).



1

Attempts to obtain the tris- or tetrakis (tetrazolyl)borate anions through reaction at higher temperatures were so far unsuccessful. Tetrazole decomposes above 170 °C. **1** is air stable and its solutions in H_2O are not hydrolyzed over at least a two-month period, as shown by NMR spectroscopy. The ^1H or ^{13}C NMR spectra of **1** show that both rings are equivalent. It was not possible, however, to decide if the tetrazolyl moiety was bonded to boron through the N-1 or N-2 position. Therefore, the structure was determined by single-crystal X-ray diffraction.

Fig. 1 shows an ORTEP [9] drawing of the anion of **1**. The equivalency of both rings in their bonding to boron is verified, and an N-1 connectivity is established. The B–N, C–N, and N–N bond lengths, as well as most bond angles are not much different from those of the bis- or tris-(pyrazolyl)borate ligands [10] or tetrazolate complexes [11]. We only note that the "inner" N–N bonds N2–N3, and N6–N7 are shorter by about 4 pm than the neighboring N–N bonds. The same effect has been observed in structures of the tetrazolate ion [11].

Fig. 2 illustrates the coordination environment for the potassium atoms in **1**. The potassium coor-

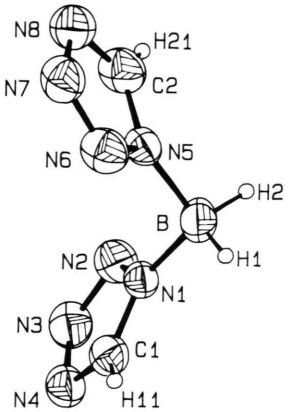


Fig. 1. Molecular structure of the $[H_2B(CHN_4)_2]^-$ anion of **1** (ORTEP, 50% probability ellipsoids for non-hydrogen atoms; arbitrary radii for hydrogen atoms). Selected distances [pm] and angles [°]: B–N1 155.3(4), B–N5 156.1(4), B–H1 110(3), B–H2 109(3), N1–N2 134.0(3), N2–N3 129.6(3), N3–N4 134.5(3), N4–C1 131.6(4), C1–N1 131.9(4), N5–N6 134.2(3), N6–N7 130.1(3), N7–N8 134.2(3), N8–C2 130.0(4), C2–N5 131.8(4), N1–B–N5 109.1(3), B–N1–N2 122.7(3), B–N1–C1 130.6(3), N1–N2–N3 107.5(2), N2–N3–N4 110.3(2), N3–N4–C1 104.9(3), N4–C1–N1 110.5(3), C1–N1–N2 106.7(3); the respective angles in the other ring are very similar.

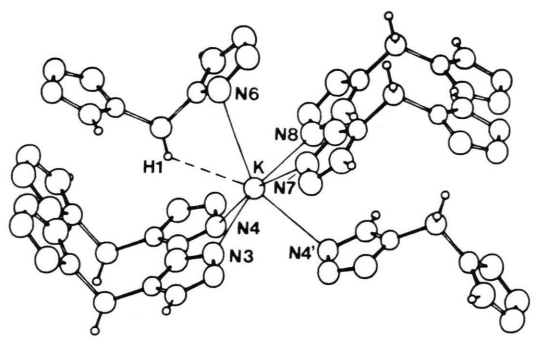


Fig. 2. Coordination sphere around potassium in **1**. Selected distances [pm] and angles [°]: K–N3 282.5(3), K–N4 290.3(3), K–N7 290.5(3), K–N8 291.4(3), K–N4′ 292.7(2), K–N6 318.0(3), K···H 289.0(30), N4′–K–N6 149.23(7), N4′–K···H 153.3(6), N6–K···H 52.0(5), N3–K–N4′ 87.73(8), N3–K–N4′ 87.11(7), N7–K–N4′ 80.86(8), N8–K–N4′ 80.29(8); the angles in the equatorial plane lie between 88.05 and 90.85 (167.94(8) for the trans nitrogens).

dination sphere consists of a distorted octahedral nitrogen polyhedron, the distortion being probably due to the coordination of a hydrogen from a B–H group. Agostic B–H···M bonds are not unusual for polypyrazolylborates containing the ligand $[H_2B(pz)_2]$ [12].

Experimental

The experiments were carried out under dried argon. – IR: Perkin-Elmer 540 B. – NMR: Bruker WP 80 SY.

Procedure A (without solvent): In a 50 ml flask equipped with a gas meter an intimate mixture of 2.16 g (40 mmol) KBH_4 and 6.17 g (88 mmol) tetrazole was heated to about 70 °C. At this temperature a brisk hydrogen evolution started, and in a few minutes about 90% (~1.8 l) of the estimated hydrogen were evolved, after which the gas evolution quickly subsided. A porous soft material was obtained. The temperature was raised to 100 °C and the reaction allowed to continue for one hour during which, however, only an additional 0.05 l of hydrogen was collected. After cooling to room temperature the solid was washed with 50 ml tetrahydrofuran (THF) to remove unreacted tetrazole. Drying *in vacuo* yielded 6.35 g (83%) of a snow-white powder.

Procedure B (with solvent): A mixture of 2.60 g (49 mmol) KBH_4 and 7.50 g (107 mmol) tetrazole was placed in a 100 ml flask equipped with a gas meter. Upon addition of 25 ml dimethylacetamide (DMA) a brisk, slightly exothermic hydrogen evolution started, and a clear solution with only a few undissolved particles formed. The solution was heated to 100 °C for 2 h during which time the gas evolution slowly continued until about 2.3 l of hydrogen were obtained. DMA was distilled off *in vacuo* and the residue was washed with 50 ml THF. Drying *in vacuo* yielded 6.90 g (74%) of a snow-white powder.

Both samples gave identical analyses: m.p. 172–178 °C with dec. (gas evolution). – IR (KBr) [cm^{-1}]: 3140 (m), 3135 (m), 2455 (s), 2315 (w), 1795 (w), 1730 (w), 1482 (m), 1471 (s), 1365 (m), 1260 (w), 1248 (w), 1235 (w), 1198 (m), 1187 (s), 1175 (m, sh), 1168 (vs), 1149 (m), 1138 (s), 1118 (vs), 1044 (m), 983 (s), 899 (m), 863 (w), 742 (m), 712 (s), 657 (w), 640 (m), 620 (w), 336 (m). – ^1H NMR (CD_3OD): δ = 8.81 s, CH; (D_2O): δ = 8.83 s (B–H signals could not be observed). – ^{13}C NMR (D_2O): δ = 148.5. Crystals were grown by slow solvent evaporation at room temperature of a concentrated methanolic solution.

$C_2H_4BN_8K$ (190.02)

Calcd C 12.64 H 2.12 N 58.97%,
Found C 12.70 H 2.07 N 58.74%.

Table I. Fractional atomic coordinates and equivalent isotropic displacement parameters for **1**; $B_{eq} = 8\pi^2/3 \sum_i \sum_j U_{ij} \mathbf{a}_i \mathbf{a}_j a_i^* a_j^*$.

Atom	x	y	z	B_{eq} [Å^2]
K	0.2682(1)	−0.03504(4)	0.7043(1)	3.27
B	0.4674(10)	0.2930(2)	0.6463(5)	3.79
H1	0.339(6)	0.307(2)	0.718(3)	4.4
H2	0.673(6)	0.295(2)	0.708(3)	4.8
N1	0.3882(5)	0.2110(1)	0.5742(3)	2.72
N2	0.5397(5)	0.1691(2)	0.5097(3)	3.75
N3	0.4238(6)	0.1030(2)	0.4661(3)	3.92
N4	0.1968(5)	0.1003(1)	0.5007(3)	3.47
N5	0.4186(5)	0.3560(1)	0.5181(3)	2.92
N6	0.1952(5)	0.3956(2)	0.4693(3)	4.10
N7	0.2168(5)	0.4433(2)	0.3631(3)	4.13
N8	0.4519(6)	0.4361(2)	0.3407(3)	4.12
C1	0.1811(6)	0.1679(2)	0.5666(4)	3.23
C2	0.5669(7)	0.3825(2)	0.4365(4)	4.03
H11	0.045(6)	0.184(2)	0.600(3)	4.6
H21	0.742(6)	0.364(2)	0.450(3)	4.9

Crystal data: $C_2H_4BN_8K$, M = 190.02, monoclinic space group $P2_1/n$ (Nr. 14) with a = 537.8(2), b = 1703.5(9), c = 919.6(3) pm, β = 106.12(3)° and V = 809.4(6)·10^6 pm^3, Z = 4, $d_{calc.}$ = 1.471 gcm^{-3}, Syntex $P2_1$, λ(Mo−Kα) = 71.069 pm, graphite monochromator, room temperature, 2118 measured reflections, 1650 unique, 1136 observed with $F_o \geq 5\sigma F_o$, hkl range: $0 \leq h \leq 10$, $0 \leq k \leq 25$, $-15 \leq l \leq 15$; ω-scan, $0° \leq 2\theta \leq 55°$, decay correction, no absorption correction, solution by direct methods (SHELXS 86); all atomic positions found and non-hydrogen atoms refined anisotropically, 125 parameters (SHELX 76), R/R_w = 0.044/0.034, Δ_{fin} (max/min) 0.237/−0.299 eA^{-3}. Positional parameters are given in Table I. Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-W-7514 Eggenstein-Leopoldshafen 2, on quoting the depository number CSD 56853, the names of the authors, and the journal citation.

This contribution has been supported by the Deutsche Forschungsgemeinschaft, by the Fonds der Chemischen Industrie, and by the Freunde der TU Berlin. We thank Mrs. M. Borowski for collecting the crystallographic data set.

[1] S. Trofimenko, Progr. Inorg. Chem. **34,** 115 (1986); K. Niedenzu and S. Trofimenko, Top. Curr. Chem. **131,** 1 (1986).
[2] For some recent references, see for example: M. Bortolin, U. E. Bucher, H. Rüegger, L. M. Venanzi, A. Albinati, F. Lianza, and S. Trofimenko, Organometallics **11,** 2514 (1992); R. Alsfasser, S. Trofimenko, A. Looney, G. Parkin, and H. Vahrenkamp, Inorg. Chem. **30,** 4098 (1991); S. G. Feng, L. Luan, P. White, M. S. Brookhart, J. L. Templeton, and C. G. Young, Inorg. Chem. **30,** 2582 (1991); K. Yoon and G. Parkin, J. Am. Chem. Soc. **113,** 8414 (1991).
[3] See for example: R. Han and G. Parkin, Inorg. Chem. **31,** 983 (1992); D. L. Reger, M. F. Huff, A. L. Rheingold, and B. S. Haggerty, J. Am. Chem. Soc. **114,** 579 (1992); C. H. Dungan, W. Maringgele, A. Meller, K. Niedenzu, H. Nöth, J. Serwatowska, and J. Serwatowski, Inorg. Chem. **30,** 4799 (1991); K. Niedenzu, H. Nöth, J. Serwatowska, and J. Serwatowski, Inorg. Chem. **30,** 3249 (1991).
[4] G. G. Lobbia, F. Bonati, and P. Cecchi, Synth. React. Inorg. Met.-Org. Chem. **21,** 1141 (1991).
[5] J. Cartwright and A. F. Hill, J. Organomet. Chem. **429,** 229 (1992); K.-B. Shiu, F.-M. Shen, S.-L. Wang, and S.-C. Wei, J. Organomet. Chem. **372,** 251 (1989).
[6] F. J. Lalor, S. M. Miller, and N. Garvey, Polyhedron **9,** 63 (1990); and references therein.
[7] M.-T. Youinou, N. Rahmouni, J. Fischer, and J. A. Osborn, Angew. Chem. **104,** 771 (1992); Angew. Chem., Int. Ed. Engl. **31,** 733 (1992); and references therein.
[8] S. Trofimenko, Inorg. Synth. **12,** 99 (1970).
[9] C. K. Johnson, ORTEP, A FORTRAN Thermal Ellipsoid Plot Program for Crystal Structure Illustrations, Report ORNL-5138, National Laboratory, Oak Ridge, Tennessee (USA) (1976).
[10] See for example: C. Lopez, R. M. Claramunt, D. Sanz, C. F. Foces, F. H. Cano, R. Faure, E. Cayon, and J. Elguero, Inorg. Chim. Acta **176,** 195 (1990); I. A. Degnan, J. Behm, M. R. Cook, and W. A. Herrmann, Inorg. Chem. **30,** 2165 (1991); D. L. Reger, S. J. Knox, M. F. Huff, A. L. Rheingold, and B. S. Haggerty, Inorg. Chem. **30,** 1754 (1991); D. L. Reger, R. Mahtab, J. C. Baxter, and L. Lebioda, Inorg. Chem. **25,** 2046 (1986).
[11] G. J. Palenik, Acta Crystallogr. **16,** 596 (1963); J. H. Bryden, Acta Crystallogr. **11,** 31 (1958); G. B. Ansell, J. Chem. Soc. Dalton Trans **1973,** 371 and references therein.
[12] S. Trofimenko, J. C. Calabrese, and J. S. Thompson, Inorg. Chem. **31,** 974 (1992); D. L. Reger, P.-T. Chou, S. L. Studer, S. J. Knox, M. L. Martinez, and W. E. Brewer, Inorg. Chem. **30,** 2397 (1991); and references therein.